



AU625757

(12) PATENT ABRIDGMENT (11) Document No. AU-B-25757/86
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 682117

(54) Title
WATER-ABSORBENT RESIN PARTICLES

International Patent Classification(s)

(51*) B01J 029/26 C08F 005/08 C08G 081/02 C08J 003/12
C08J 003/14 C08J 003/16 C08L 033/02

(21) Application No. : 25757/85

(22) Application Date : 31.05.85

(87) PCT Publication Number : WO85/33558

(30) Priority Data

(31) Number (32) Date (33) Country
6-168631 05.05.84 JP JAPAN
6-268283 05.10.84 JP JAPAN

(43) Publication Date : 04.01.86

(44) Publication Date of Accepted Application : 18.09.87

(71) Applicant(s)
SANYO CHEMICAL INDUSTRIES, LTD.

(72) Inventor(s)
MASASHI DATE; MASAHISA FUJITA; TAKASHI SUMIYA; MASANORI KOKE; KENJI TANAKA

(74) Attorney or Agent
DAVIES COLLISON CAVE, 1 Little Collins Street, MELBOURNE VIC 3000

(57) Claim

1. Improved water-absorbent resin particles comprising water-absorbent resin particles (A) which are a crosslinked polymer of ethylenically unsaturated monomers comprising acrylic acid and/or acrylic acid salt as an essential element, treated with an organic polysiloxane (B) which is in the liquid state at an ordinary temperature, wherein

- ① (A) and (B) are mixed and/or reacted,
- ② the ratio of particles with a particle size of 10 - 1,000 μ m in (A) particles is 95 weight % or more,
- ③ the weight ratio of (A)/(B) is 100/(0.001-5).

BEST AVAILABLE COPY

DESCRIPTION

IMPROVED WATER-ABSORBENT RESIN PARTICLES

Technical Field

The present invention relates to water-absorbent resin particles treated with organic polysiloxane. More specifically, it relates to improved water-absorbent resin particles treated with liquid organic polysiloxane to have an improved absorption rate with little problem of blocking caused by moisture absorption.

Background Art

Hitherto water-absorbent resins have been broadly used in hygienic materials such as sanitary napkins and disposable diapers or water retaining materials for soil. Examples of such water-absorbent resins include substantially water-insoluble crosslinked polymers such as crosslinked polyacrylic acid salts, self-crosslinked polyacrylic acid salts, crosslinked graft-copolymers of starch-acrylic acid salts, crosslinked copolymers of vinyl alcohol-acrylic acid salts, hydrolyzed crosslinked copolymers of acrylamide, neutralized crosslinked copolymers of isobutylene-maleic anhydride and crosslinked carboxymethyl cellulose salts.



Although such conventional water-absorbent resins have a high absorbing ability, they are not satisfactory enough for the applications in disposable diapers or sanitary napkins, which require a high absorption rate, and thus water-absorbent resins in a particle form have been commonly used in combination with a fibrous material having a high absorption rate such as pulp.

That is, there has been a problem that since as the absorbing ability of a water-absorbent resin increases the affinity with water increases as well, when the resin particles come in contact with water, the contacted portion is gelatinized to prevent uniform penetration of water to the inner part of particles, resulting in a lower absorption rate.

In order to rectify the problem, attempts have been made to increase the surface area by crushing water-absorbent resin particles to increase the area contacting water to facilitate the absorption rate. By increasing the surface area, absorption rate becomes somehow higher. However, since a film of undissolved powder lump is formed at a surface portion of resin particles in contact with water, and further particles stick to each other to deteriorate the uniform penetration of water, merely crushing particles did not lead to fundamental improvement of the absorption rate.

In addition to the above mentioned problem, in conventional water-absorbent resin particles, the high absorbing property



causes problems such as blocking of the water-absorbent resin particles to each other caused by absorbing moisture to adhere to the machine, or disabling the discharge of the water-absorbent resin from the hopper or continuous regular supply to the machine in the process of storing or providing the water-absorbent resin particles to the machine for producing disposable dispers in conditions of high humidity.

As the means to improve the hygroscopic blocking rate, methods as the following examples ①-④ have been proposed hitherto.

① a method of mixing hydrophobic silica fine particles having an average particle size of $0.05 \mu\text{m}$ or smaller and a specific surface area of $50 \text{ m}^2/\text{g}$ or greater to the water-absorbent resin particles as disclosed in the Japanese Patent Application Laid Open No. 133028/1981.

② a method of adding inorganic powders such as hydrated silicon dioxide, hydrated aluminum hydroxide and hydrated titanium hydroxide to the water-absorbent resin particles as disclosed in the Japanese Patent Application Laid Open No. 80459/1984.

③ a method of treating the water-absorbent resin particles with a cationic surface active agent and further adding organic compound powders having a high melting point as disclosed in the Japanese Patent Application Laid Open No. 69854/1986.



④ a method of mixing stearic acid and inorganic powders to the water-absorbent resin particles to form a film of stearic acid on the surface of the water-absorbent resin particles as disclosed in the Japanese Patent Application Laid Open No. 105064/1988.

However, although in the method ① adding a hydrophobic silica contributes to improving the hygroscopic blocking rate, it has problems such as reducing the absorption rate, initial absorbency under load and absorbing capacity due to the surface of the water-absorbent resin particles being covered with the hydrophobic silica, or generating much dust due to the mixed fine powders of silica.

In the method ② when the inorganic powders are not hydrophobic, although it does not reduce the initial absorbency under load or absorbing capacity, it has problems such as insufficient improvement of the hygroscopic blocking rate, generating much dust due to the mixed fine powders of inorganic silica like the method ①. Further, when the inorganic powders are hydrophobic, there is the same problem as the method ①.

The methods ③ and ④ of covering the surface of the water-absorbent resin particles with a hydrophobic organic compound having a high melting point or stearic acid improve the hygroscopic blocking rate to some extent but not sufficiently. Besides, they have problems such as reducing the initial



absorbency under load and the absorbing capacity due to the organic compound having a high melting point or the stearic acid hindering the absorbing property of the water-absorbent resins.

Accordingly, a first object of the present invention is to provide water-absorbent resin particles having a high absorption rate by promoting uniform penetration of water, urine or menstrual blood to the inner part of water-absorbent resin particles by improving the water-absorbent resin particles.

Further, a second object of the present invention is to provide water-absorbent resin particles having a lower hygroscopic blocking rate and dust level, and an excellent initial absorbency under load and absorbing capacity by solving problems of the above mentioned methods ①-④ for improving hygroscopic blocking rate by improving water-absorbent resin particles.

Disclosure of Invention

The present invention is to provide improved water-absorbent resin particles produced by treating substantially water-insoluble water-absorbent resin particles (A), which are crosslinked polymers of ethylenically unsaturated monomers comprising acrylic acid and/or acrylic acid salt as an essential element, with an organic polysiloxane (B) which is in the liquid state at an ordinary temperature, wherein



- ① (A) and (B) are mixed and/or reacted,
- ② the ratio of particles with a particle size of 10-1,000 μ m in (A) particles is 95 weight % or more,
- ③ the weight ratio of (A)/(B) is 100/(0.001 to 3).

That is, improved water-absorbent resin particles of present inventors are improved by treating the water-absorbent resin (A) with the organic polysiloxane (B), and by this treatment, (B) adheres to the surface of (A) particles, or (B) is affixed to the surface of (A) particles by the reaction of (A) and (B). According to whether (A) and (B) are reactive or not, they will be in the mixed state or the reacted state.

In either state, since the surface of (A) particles is improved with (B) liquid organic polysiloxane, the water-absorbent resin particles of the present invention have an improved hygroscopic blocking rate in a high humidity and obtain a wettability to prevent the generation of dust.

Further, since a conventional disadvantage of disturbing uniform penetration of water caused by bonding of water-absorbent particles each other is improved by the modification effect of (B) in this invention, the absorption rate is improved.

Further, improved water-absorbent resin particles of the present inventors also have an excellent initial absorbency under load and absorption ability.



Best Mode for Carrying Out the Invention

The water-absorbent resin particles (A) of the present invention are substantially water-insoluble water-absorbent resin particles which absorb a considerable amount of water when in contact with water to swell and form a water-containing gel (hydrogel). Such water-absorbent resins (A) are crosslinked polymers of ethylenically unsaturated monomers comprising acrylic acid and/or acrylic acid salt as an essential element.

Examples of such water-absorbent resins (A) include crosslinked partially neutralized polyacrylic acid, self-crosslinked partially neutralized polyacrylic acid, crosslinked graft-copolymers of starch-acrylic acid salt, hydrolyzed crosslinked graft-polymers of starch-acrylonitrile, crosslinked copolymers of vinyl alcohol-acrylic acid salt, hydrolyzed crosslinked copolymers of acrylic acid-acrylamide, hydrolyzed crosslinked copolymers of acrylic acid salt-acrylonitrile, crosslinked copolymers of acrylic acid salt and 2-acrylamide-2-methyl propane sulfonate, neutralized crosslinked copolymers of isobutylene-maleic anhydride, and mixture of two or more of these examples.

In the case when the above mentioned crosslinked polymers shown as examples of the water-absorbent resins (A) are formed with carboxylic salts such as acrylic acid salt as a raw material, or when they form salts as a neutralized product or a



partially neutralized product. examples of such salts include sodium salt, potassium salt, ammonium salt and amine salt. Among them, sodium salts and potassium salts are preferable.

Among the above mentioned examples of the water-absorbent resins (A), crosslinked partially neutralized polyacrylic acid, self-crosslinked partially neutralized polyacrylic acid, crosslinked graft-copolymers of starch-acrylic acid salt and crosslinked copolymers of vinyl alcohol-acrylic acid salt are preferable in consideration of the absorbing characteristics of the water-absorbent resins when they are applied as finished products.

It is preferable to use a water-absorbent resin as the water-absorbent resin (A) having absorbing performance to physiological saline (0.9 % aqueous solution of sodium chloride) in general of 30 times or more of self weight, preferably 35 - 80 times, more preferably 40 - 70 times.

As to the particle size distribution of the water-absorbent resins (A), it is necessary to use water-absorbent resin particles with the particle size distribution having 95 weight % or more of particles with the size of 10 - 1,000 μ m, preferably water-absorbent resin particles with the particle size distribution having 95 weight % or more of particles with the size of 50 - 850 μ m among (A) particles. Since water-absorbent resin particles with the particle size distribution having less



than 95 weight % of particles with the size of 10 - 1,000 μ m containing much particles having a smaller particle size tend to form lumps at the time of water absorption to deteriorate the absorption rate, it is not preferable. On the other hand, since water-absorbent resin particles having particle size distribution containing much particles with a larger size take long time to absorb water to the inner part of particles to similarly deteriorate the absorption rate, it is not preferable. Although an average particle size is not particularly limited, it is preferably 200 - 600 μ m.

The shape of the water-absorbent resin (A) particles is not particularly limited and examples include spherical shape obtained in reversed phase suspension polymerization, lamellar shape obtained in drum drying, block shape or random shape obtained in pulverizing a resin lump and agglomerates of such particles.

The organic polysiloxane (B) in the present invention includes ones in a liquid state in an ordinary temperature regardless of whether they are reactive with the water-absorbent resin (A) or not. That is, examples of (B) include ones which are reactive with carboxylic acid (salt) group in the water-absorbent resins (A) and ones which are not (Here "carboxylic (salt) group" denotes carboxyl group and/or carboxylic salt group and similarly used hereinafter.). However, since organic



silicone monomers called silane coupling agents are, in general, monomers with comparatively low molecular weight and can not provide a targeted advantages merely by blending, they are not suitable as the organic polysiloxane (B).

Examples of (B) having no reactivity with (A) include dimethyl silicone oil, methyl hydrogen silicone oil, methyl phenyl silicone oil, cyclic dimethyl silicone oil, polyether-modified silicone oil, carboxyl-modified silicone oil, alkyl-modified silicone oil and alkoxy-modified silicone oil. These can be used in combination of two or more. Also emulsion formed by emulsifying these in water can be used preferably in this invention.

Examples of (B) having reactivity with (A) include silicone oils having at least one functional group which can react with a carboxylic (salt) group of (A). Concrete examples include amino-modified silicone oil, epoxy-modified silicone oil, carbinol-modified silicone oil, phenol-modified silicone oil and mercapto-modified silicone oil.

Among examples of those having no reactivity with (A), preferable are dimethyl silicone oil and polyether-modified silicone oil with respect to availability at a low price.

Among examples of those having reactivity with (A), preferable are amino modified silicone oil and epoxy-modified silicone oil with respect to reactivity with carboxylic (salt)



group at a relatively low temperature. Particularly preferable is amino-modified silicone oil with respect to reactivity with carboxylic (salt) group at an ordinary temperature.

Examples of the amino-modified silicone oil include an amino-modified silicone oil which has a group illustrated as $-R^1NR^2R^3$ (Herein R^1 denotes an alkylene group of 1 to 12 carbon atoms; R^2 , R^3 denote H or an alkyl group of 1 to 12 carbon atoms. One or more hydrogen atoms in the alkylene group and/or alkyl group can be substituted by an OH group, a COOH group or an NH_2 group and the like. When the number of the carbon atoms is two or more, an ether linkage having an oxygen atom between carbon-carbon bonds can be included.) at an end of the silicone polymer molecules and/or in the molecules.

Examples of the epoxy-modified silicone oil include an epoxy-modified silicone oil which has a group illustrated as $-RX$ (Herein R denotes an alkylene group of 1 to 12 carbon atoms; X denotes an epoxy group. One or more hydrogen atoms in the alkylene group can be substituted by an OH group, a COOH group and the like. When the number of the carbon atoms of the alkylene group is two or more, an ether linkage having an oxygen atom between carbon-carbon bonds can be included.) at an end of the silicone polymer molecules and/or in the molecules.

In comparing those having reactivity with (A) and those not having reactivity with (A) among the above mentioned (B), those



having reactivity are more preferable with respect to unsusceptibility of detaching from the surface of the resin particles at moisture absorption and expectancy that those having adherence to (A) have a greater modification effect with less amount to apply.

Among the above mentioned (B), functional groups of an organic polysiloxane which can react with (A) are one or more per molecule of the modified silicone oil. However, the number of the functional groups is preferably two or more in order to also crosslink the vicinity of the surface of the resin particles. And more preferably the number of reactive functional groups is from 2 - 20 for the efficient crosslinking. A functional group can be positioned either at an end, at a side chain, or at both an end and a side chain of the silicone polymer.

An organic polysiloxane can be used as the organic polysiloxane (B) as long as it is in a liquid state in an ordinary temperature and molecular weight thereof is not particularly limited, but preferably is 1,000 or more, more preferably 3,000 or more. The upper limit of the molecular weight of the organic polysiloxane (B) is not particularly limited but it is in general about 1,000,000. Since progressive deterioration of the hygroscopic blocking rate or the dust level can be avoided by using an organic polysiloxane having a molecular weight of 1,000 or more, it is preferable.



The surface tension of the organic polysiloxane (B) is not particularly limited, but is preferably 18 - 30 dyne/cm, more preferably 20 - 26 dyne/cm. Since penetration of (B) to the inside of water-absorbent resin particles can be prevented and thereby economical without the need of using much (B) and without susceptibility of deteriorating absorbing performance for increased water repellent effect, it is preferable. Further, since there is not susceptibility of deteriorated particle fluidity or generation of blocking, it is preferable. The surface tension is the value measured at 25 °C.

The viscosity of (B) is not particularly limited as long as it is in a liquid state in an ordinary temperature, but preferably is from 10 - 20,000 centistokes (cst) at an ordinary temperature (25 °C), particularly preferably is from 30 - 1,000 cst with respect to not having the need to dilute with a solvent and thus easily being mixed with (A).

Using an organic polysiloxane with the viscosity in the above mentioned range is preferable for the reasons that there is no need to add a step of diluting with an organic polysiloxane of a low viscosity or other solvents such as methyl ethyl ketone, cellosolves and lauryl alcohol or a step of eliminating the solvent used for dilution after blending treatment with (A), thereby economical, that particle fluidity can be maintained preferably, and that (B) becomes barely penetrate to the inside



of water-absorbent resin particles to eliminate the need of using a great deal of (B) to obtain the desired effect and thus (B) does not become a binder of (A) particles to delay the absorption rate or generate blockings. The viscosity is the value measured at 25 °C.

The amount of the organic polysiloxane (B) to the water-absorbent resin particles (A) can vary, but the weight ratio of ((A) particles : (B)) is, in general, (100 : 0.001-5), preferably (100 : 0.001-3), more preferably (100 : 0.01-1).

If the ratio of (B) is less than 0.001, the effect on the hygroscopic blocking rate is insufficient, and thus a water-absorbent resin composition with an improved water absorption rate cannot be provided.

On the other hand, if the ratio exceeds 5, although it is effective in terms of improvement of the absorption rate, since other problems such as deterioration of absorbing performance, insufficiency of particle fluidity, and generation of blocking, it can not be used practically.

Further, the water-absorbent resin (A) particles used in the present invention which are further treated with a crosslinking agent having at least two functional groups reactive with carboxylic (salt) group for treating the vicinity of the surface of (A) particles for modification in addition to the treatment with (B) for modification can be preferably used in this



invention since the absorption rate can further improve and the gel strength increases.

The timing of surface crosslinking of (A) particles with a crosslinking agent (C) is not particularly limited, and any time before the treatment of (A) particles with (B), at the time of the treatment with (B), and after the treatment with (B) can be applied.

The kind of the crosslinking agent (C) varies according to the kind of the water-absorbent resin (A) used and the kind of the organic polysiloxane (B), but for example, polyglycidyl ether compounds, polyol compounds, polyamine compounds, polyamine resins, carbonate compounds, haloeipoxy compounds and polyaldehyde compounds can be used.

Concrete examples of polyglycidyl ether compounds include ethylene glycol diglycidyl ether, glycerol-1,3-diglycidyl ether, glycerol triglycidyl ether, polyethylene glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether and polyglycerol polyglycidyl ether.

Concrete examples of polyol compounds include glycerol, ethylene glycol, polyethylene glycol, polypropylene glycol and diethanol amine.

Concrete examples of polyamine compounds include ethylene diamine, diethylene triamine and triethylene tetramine.

Concrete examples of polyamine resins include polyamide



polyamine epichlorohydrin resin and polyamine epichlorohydrin resin.

Concrete examples of carbonate compounds include ethylene carbonate.

Concrete examples of haloeпоxy compounds include epichlorohydrin and α -methyl epichlorohydrin.

Concrete examples of polyaldehyde compounds include glutaraldehyde and glyoxal.

Among the examples of the crosslinking agents (C), polyglycidyl ether compounds, polyol compounds and polyamine resins are preferable with respect to the ability to obtain water-absorbent resin particles excellent in both absorption rate and gel strength by forming a strong covalent bond with a carboxylic acid (salt) group. Ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, glycerol-1,3-diglycidyl ether, glycerol triglycidyl ether, polyamine epichlorohydrin resin and polyamide polyamine epichlorohydrin resin are more preferable with respect to their low reaction temperature, thereby economical in terms of energy cost.

The amount of the crosslinking agent (C) can vary depending upon the kind of the crosslinking agent (C), the kind and the crosslinking degree of the water-absorbent resin (A) and the desired performance of the improved water-absorbent resin to obtain in this invention, but the weight ratio of (water-



absorbent resin (A) : crosslinking agent(C)) is, in general, (100 : 0.001-5), preferably (100 : 0.001-3), more preferably (100 : 0.01-2) and most preferably (100 : 0.05-1). It is preferable to use a crosslinking agent (C) in the above-mentioned range since it further improve the absorption rate of the water-absorbent resin particles and increase the gel strength without the problem of the deterioration of the absorbing amount.

The method of adding (B) [and the above mentioned crosslinking agent (C) optionally added] can be any method as long as a prescribed amount is added. Examples of such methods include :

- a) a method of blending each component directly,
- b) a method of preparing a master batch in advance by adding (B) having a high concentration (such as 5-20 weight % concentration) into (A) and blending, followed by adding and blending the master batch to (A) to adjust the concentration of (B) to be a prescribed amount.
- c) a method of adding an emulsion of (B) to (A) particles and blending.
- d) a method of dispersing or dissolving (B) [and a crosslinking agent (C) optionally added] in a hydrophobic organic solvent and/or a hydrophilic organic solvent and then adding to (A) particles and blending, and
- e) a method of dissolving or dispersing (B) [and a



crosslinking agent (C) optionally added] in a solvent mixture comprising water and a hydrophilic organic solvent such as alcohol followed by adding and blending.

As the device used to add (B) [and a crosslinking agent (C) optionally added] to (A) particles, an ordinary blender such as a cylindrical blender, a screw blender, a screw extruder, a turbulizer, a Nauta blender, a V-shaped rotating mixer, a ribbon blender, a double arm type kneader, a fluidized bed mixer, an air blender, a rotating disc type mixer, a conical blender and a roll mixer can be used.

A mixture obtained by the above-mentioned process can be heated to promote the reaction if necessary, depending on the existence of reactive functional groups and the reactivity of the functional groups in (B) [and the crosslinking agent (C) optionally added]. The above mentioned blending and heating can be conducted simultaneously. The reaction herein denotes a crosslinking reaction between the "water-absorbent resin (A)" and the "modified silicone oil when a modified silicone oil reactive with (A) is used and the crosslinking agent (C) optionally added".

The temperature of the heating is in general, 60 - 200 °C, preferably 80 - 180 °C. For the heating, a drier or a heater such as a hot-air drier, a rotary drier, a paddle drier, a rotating disc drier, a fluidized bed drier, a belt type drier, a



Nauta type drier and an infrared drier can be used.

To improved water-absorbent resin particles of the present invention, silicon dioxide fine powders (D) can be added at an optional stage of the modification treatment. By adding (D), the absorption rate can be further improved. Further, improvement of the particle fluidity can be expected.

Examples of silicon dioxide fine powders (D) include a dry inorganic silica produced by hydrolyzing silicon tetrachloride in the flame of combusting oxygen and hydrogen at a high temperature, which is generally called "Fumed Silica". Further, silica having an alkyl group introduced by further reacting a silanol group at the surface of an inorganic silica with a silane such as monomethyl trichlorosilane, dimethyl dichlorosilane and trimethyl chlorosilane can be used as well. Concrete examples include silicon dioxides having a specific surface area of 50 - 500 m²/g with the particle size of the primary particle of 5 - 50 nm.

Preferable examples of silicon dioxide fine powders (D) include so called hydrophilic silicon dioxides having a specific surface area and a particle size in the above mentioned range with the hydrophilic degree of 70 % or more. Here "hydrophilic degree" denotes the weight ratio of silicon dioxide suspended colloiddally in the mixed solution of water/methanol = 70/30 (weight ratio). As the value becomes smaller the hydrophobic



property becomes stronger. Those which are generally called hydrophobic silica are silicon dioxide having the hydrophilic degree of 0 %. As the hydrophobic property becomes stronger, the absorption rate of the water-absorbent resin particles tends to deteriorate, although it partly depends on the amount of (B) added to (A). therefore it is preferable to use a hydrophilic silicon dioxide having a hydrophilic degree of 70 % or more.

An amount of silicon dioxide fine powders (D) to the amount of (A). when used, is in general 0.001 - 2 weight %, preferably 0.01 - 1 weight part, and more preferably an amount smaller than the amount of (B) added to (A). By adding (D) in an amount in the above mentioned range, the absorption rate can be further improved without the problem of dust generation and the particle fluidity can be expected to be further improved.

Methods of adding a silicon dioxide fine powder (D) include, for example, a method of adding and blending (D) to (A) particles in advance, a method of adding and blending (D) to (B), a method of adding (D) while blending (A) particles and (B) and a method of adding and blending (D) to a mixture of (A) particles and (B).

To the improved water-absorbent resin particles of the present invention, fillers or additives may be included if necessary as long as it does not disturb the effect of the present invention. Examples of such fillers or additives include organic powders (such as pulp powders, cellulose derivatives and



natural polysaccharides). inorganic powders (such as zeolite, silica, alumina, bentonite and active carbon). antioxidants. antiseptic agents. disinfectants. surface active agents, coloring agents, perfumes and deodorants. The amount of these is, in general, 10 weight % or less with respect to the weight of the improved water-absorbent resin particles.

Improved water-absorbent resin particles of the present invention are substantially water-insoluble resin particles, and the hygroscopic blocking rate, dust level and absorbing characteristics can be controlled according to the intended application thereof. ① The hygroscopic blocking rate in high humidity (of 40 °C, 80 % RH, after three hours) is in general, 20 % or less, preferably 10 % or less. ② The dust level is in general, 10 cpm or less, preferably 5 cpm or less. ③ The initial absorbency under load to physiological saline solution is 20 g/g or more, preferably 25 g/g or more. The upper limit of the amount of the initial absorbency is not particularly limited and greater is better, but in general, 50 g/g or smaller.

Physiological saline solution herein denotes an aqueous solution of sodium chloride (concentration of 0.85 - 0.95 weight %).

Since the water-absorbent resin particles of the present invention do not cause hygroscopic blocking under high humidity nor generate dust in the production process of disposable



diapers, etc. and have a good initial absorbency under load, a good dryness of the gel after absorption and smooth feeling can be provided. Therefore, for example, when applied in a disposable diaper, they absorb great amount of urine quickly while enduring the load such as the weight of the baby to provide a good surface dryness of the disposable diaper after urination.

Although the present invention will be further explained referring to examples and comparative examples, the present invention is not limited thereto.

<Examples 1-4, Comparative Examples 1-7>

The hygroscopic blocking rate, the dust level, the initial absorbency under load and the absorbing capacity under load of Examples 1-4 and Comparative Examples 1-7 were measured by the method described below. Hereinafter "%" refers to "weight %" unless specifically noted.

Hygroscopic blocking rate :

10 g of water-absorbent resin particles having a particle distribution of 20 mesh or less were placed evenly in an aluminum plate having a diameter of 5 cm. The plate was left in a temperature controlled and humidity controlled chamber at 40 °C and a relative humidity of 80 % for three hours. Then the water-absorbent resin particles were sieved with a 12-mesh metal screen lightly, the weight of the resins which became 12 mesh or more by



hygroscopic blocking was measured, and the hygroscopic blocking rate was calculated by the following formula.

Hygroscopic blocking rate (%)

= (weight of the resins of 12 mesh or more)/(total weight of the resin particles after being left) \times 100

Dust level :

The inhalation top of a one-liter suction bottle was connected to a sampling opening of a digital dust counter manufactured by Shibata Kagaku Co. Ltd. with a glass tube having 7 mm bore and 10 cm length. 20 g of water-absorbent resin particles were dropped into the suction bottle from the top by means of a funnel. The number of the dust particles generated from the dropped water-absorbent resin particles per one minute was measured with the digital dust counter and the value was defined as the dust level [unit cpm (count per minute)].

Initial absorbency under load and absorption rate :

0.1 g of the water-absorbent resin particles were spread evenly in a cylindrical plastic tube (30 mm bore, 60 mm height) having 250-mesh nylon net at the bottom and a 30 mm diameter weight was placed on the water-absorbent resin particles so that a load of 20 g/cm² was applied thereto.

The plastic tube containing the water-absorbent resin particles was placed to be soaked in a Petri dish (12 cm diameter) containing 60 ml of physiological saline solution. with



the side having nylon net down, and then left. The increased weight of the water-absorbent resin particles was measured after absorbing the physiological saline solution for 10 minutes and 60 minutes respectively. The value 10 times as much as the increased weight after 10 minutes was defined as the initial absorbency under load to physiological saline solution, and the value 10 times as much as the increased weight after 60 minutes was defined as the absorbing capacity under load to physiological saline solution.

Example 1

100 g of commercially available water-absorbent resin particles "SANWET IM-5000D" [partially sodium neutralized salt of crosslinked polyacrylic acid produced by Sanyo Chemical Industries, Ltd.: having particles with the size of 10 - 1,000 μ m for 99.9 weight or more] were placed in a polyvinylchloride bag and 0.2 g of an amino-modified silicone oil [produced by Shin-Etsu Chemical Co., Ltd. as "KF-880" (surface tension 21.3 dyne/cm; viscosity 550 cps; average molecular weight approximately 20,000)] was added thereto and mixed thoroughly to obtain improved water-absorbent resin particles (a1) of the present invention. The measured results of the performance of the resin particles are described in the Table-1.

Example 2

100 g of water-absorbent resin particles commercially



available as "SANWET IM-5800" [surface crosslinked partially sodium neutralized salt of crosslinked polyacrylic acid produced by Sanyo Chemical Industries, Ltd.; having particles with the size of 10 - 1,000 μ m for 99.9 weight or more] were placed in a 2,000-ml juicer-mixer and while mixing 0.5 g of an epoxy-modified silicone oil [produced by Shin-Etsu Chemical Co., Ltd., as "KF-101" (surface tension 25.2 dyne/cm; viscosity 2,000 cps; average molecular weight approximately 9,000)] was added thereto and mixed thoroughly. The obtained mixture was heated at 150 °C for approximately 20 minutes to obtain improved water-absorbent resin particles (a2) of the present invention. The measured results of the performance of the resin particles are described in the Table-1.

Example 3

100 g of water-absorbent resin particles commercially available as "SANWET IM-1000" [partially sodium neutralized salt of graft-polymers of starch-acrylic acid, produced by Sanyo Chemical Industries, Ltd.; having particles with the size of 10 - 1,000 μ m for 99.9 weight or more] were placed in a 2,000-ml juicer-mixer and while mixing 5 g of an aqueous solution of methanol which was obtained by dissolving 6 weight % of an epoxy-modified silicone oil [produced by Shin-Etsu Chemical Co., Ltd., as "KF-101"] and 2 weight % of ethylene glycol diglycidyl ether [produced by Nagase Kasei Kogyo Co. Ltd., as "Denacol EX-810"] in



an 80 weight % aqueous solution of methanol (the ratio corresponds to 0.3 part of "KF-101" and 0.1 part of "EX-810" to 100 parts of water-absorbent resin particles, respectively) was added thereto and mixed thoroughly. The obtained mixture was heated at 150 °C for approximately 20 minutes to obtain improved water-absorbent resin particles (a3) of the present invention. The measured results of the performance of the resin particles are described in the Table-1.

Example 4

100 g of "SARWET IM-1000" was placed in a 2,000-ml juicer-mixer and while mixing 5 g of an aqueous solution which was obtained by dissolving 0.1 g of an epoxy-modified silicone oil [produced by Shin-Etsu Chemical Co., Ltd., as "X-22-163B" (surface tension 21.0 dyne/cm; viscosity 65 cps; average molecular weight approximately 3,000)] and 6 weight % of polyamine epichlorohydrin resin in 30 weight % aqueous solution of ethylene oxide 3 mole adducts of methanol (the ratio corresponds to 0.1 part of "X-22-163B" and 0.3 part of polyamine epichlorohydrin resin to 100 parts of water-absorbent resin particles, respectively) was added thereto and mixed thoroughly. The obtained mixture was heated at 150 °C for approximately 20 minutes to obtain improved water-absorbent resin particles (a4) of the present invention. The measured results of the performance of the resin particles are described in the Table-1.



Comparative Example 1

The commercially available "SANWET IM-5000D" was used as the comparative water-absorbent resin particles (b1). The measured results of the performance of the resin particles are described in the Table-1.

Comparative Example 2

The commercially available "SANWET IM-5800" was used as the comparative water-absorbent resin particles (b2). The measured results of the performance of the resin particles are described in the Table-1.

Comparative Example 3

The commercially available "SANWET IM-1000" was used as the water-absorbent resin particles (b3). The measured results of the performance of the resin particles are described in the Table-1.

Comparative Example 4

0.5 g of a hydrophobic silica ("Aerosil-972") was added to 100 g of commercially available particle type water-absorbent resin "SANWET IM-5000D" to obtain the comparative water-absorbent resin particles (b4). The measured results of the performance of the resin particles are described in the Table-1.

Comparative Example 5

1.0 g of titanium oxide having the particle size of 30 μ m was added to 100 g of commercially available particle type water-



absorbent resin "SANWET IM-5000D" to obtain the comparative water-absorbent resin particles (b5). The measured results of the performance of the resin particles are described in the Table-1.

Comparative Example 6

5 g of distearyl dimethyl ammonium chloride was melted by heating and was added to 100 g of commercially available particle type water absorbent resin "SANWET IM-5800" and stirred at 80 °C for 10 minutes. Then 0.5 g of polystyrene powders having the particle size of 20 μ m were added thereto to obtain the comparative water-absorbent resin particles (b6). The measured results of the performance of the resin particles are described in the Table-1.

Comparative Example 7

1 g of stearic acid was added to 100 g of commercially available particle type water-absorbent resin "SANWET IM-5800" and heated at 80 °C to melt the stearic acid for 10 minutes with stirring. Then 3 g of silicon oxide was added thereto and mixed thoroughly and cooled to room temperature to obtain the comparative water-absorbent resin particles (b7). The measured results of the performance of the resin particles are described in the Table-1.



Table-1

	water-absorbent resin particles	hygroscopic blocking rate (%)	dust level (cps)	initial absorbency under load (g/g)	absorbing ability under load (g/g)
Example 1	(a1)	5	0	26	34
Example 2	(a2)	3	2	31	38
Example 3	(a3)	1	4	32	37
Example 4	(a4)	0	2	31	36
Comparative Example 1	(b1)	95	60	15	30
Comparative Example 2	(b2)	90	50	24	35
Comparative Example 3	(b3)	98	70	3	10
Comparative Example 4	(b4)	13	210	8	21
Comparative Example 5	(b5)	70	980	12	27
Comparative Example 6	(b6)	40	80	16	27
Comparative Example 7	(b7)	30	40	13	28



The following facts were learned from Table-1.

① The improved water-absorbent resin particles (a1)-(a4) of the present invention have dramatically improved hygroscopic blocking rate, dust level, initial absorbency under load and absorbing capacity compared to the untreated water-absorbent resin particles (b1)-(b3).

② The improved water-absorbent resin particles (a1)-(a4) of the present invention have superior hygroscopic blocking rate, dust level, initial absorbency under load and absorbing capacity compared to the comparative water-absorbent resin particles (b4)-(b7).

③ Further, although the comparative water-absorbent resin particles (b4)-(b6) were improved in terms of hygroscopic blocking rate in comparison with the untreated water-absorbent resin particles (b1)-(b3), they became inferior in terms of dust level. Moreover, all of the comparative water-absorbent resin particles (b4)-(b7) became inferior to the untreated water-absorbent resin particles (b1)-(b3) in terms of the initial absorbency under load and the absorbing capacity.

<Examples 5-16, Comparative Examples 8-12>

The absorbency under pressure-free state, absorbency under load, absorption rate, permeability and gelling time were measured by the method described below.

Absorbency under pressure-free state:



1 g of water-absorbent resin particles were placed in a tea bag (with length : 20 cm, width : 10 cm) made from 250-mesh nylon net and was then soaked in 500 ml of physiological saline solution (0.9 % aqueous solution of sodium chloride) for 30 minutes and taken out and left for water removal for 15 minutes. Then, the weight increase was measured and the value was defined as the absorbency under pressure-free state.

Absorbency under load:

In a cylindrical plastic tube (30 mm bore, 60 mm height) with a 250-mesh nylon net affixed on the bottom side, 0.1 g of water-absorbent resin particles were placed and spread evenly, and a weight with 30 mm outside diameter was placed so that 20 g/cm² load was applied. A plastic tube containing the water-absorbent resin particles was soaked in a Petri dish (diameter : 12 cm) containing 60 ml of physiological saline solution, and left with the nylon net side down for 30 minutes. The 10-fold value of the increase in weight after 30 minutes was defined as the absorbency under load.

Absorption rate:

50 ml of physiological saline solution and a magnetic rotating element (approximately column shape with length of 30 mm, diameter of 8 mm in the center, diameter of 7 mm at both ends) were placed in a 100 ml beaker and 2 g of water-absorbent resin particles were introduced with rotating the magnetic



rotating element at 600 rpm by a magnetic rotator. The time taken from immediately after the introduction to the stoppage of rotation of the magnetic rotating element was measured and defined as the absorption rate.

Permeability:

2 g of water-absorbent resin particles were placed in a 50 ml beaker and 30 ml of physiological saline solution was added thereto slowly so as not to cause dispersion of the water-absorbent resin particles. Then the permeation state of the physiological saline solution to the inside of the water-absorbent resin particles was judged by eyes. The criteria of the judgment are as follows.

- ◎ : Good permeability without lump formation
- : Good permeability but with few lump formation
- △ : Slightly poor permeability with lump formation
- × : Poor permeability with lump formation entirely

Gelling time :

2 g of water-absorbent resin particles were placed in a 50 ml beaker and 30 ml of physiological saline solution was added thereto slowly so as not to cause dispersion of the water-absorbent resin particles. Then the time until when the entire liquid becomes gelled without fluidity was measured and the value was defined as the gelling time.

Comparative Example 8



95 g of sodium acrylate, 27 g of acrylic acid, 0.3 g of N,N'-methylene bisacryl amide and 430 g of deionized water were placed in a 1 liter glass reactor and the temperature of the contents was kept at 5 °C with stirring and mixing. After introducing nitrogen to the contents to have the dissolved oxygen amount of 1 ppm or less, 1 g of 1 % aqueous solution of hydrogen peroxide and 1 g of 0.3 % aqueous solution of ascorbic acid were added to start polymerization. After the polymerization of approximately 5 hours, a hydrogel polymer was obtained. The hydrogel polymer was dried by hot air at 130-150 °C, and was pulverized to the particle distribution of the particle size of 850 μ m or smaller to obtain the water-absorbent resin particles (b9). (b8) contains 7.2 % of fine particles with the particle size of 105 μ m or smaller, and 1.0 % of fine particles with the particle size of 45 μ m or smaller. The measured results of the performance of the water-absorbent resin particles (b8) are described in the Table-2.

Comparative Example 9

While 100 g of the water-absorbent resin particles (b8) obtained in the Comparative Example 8 was stirred at high speed, 1 g of 10 % aqueous solution of ethylene glycol diglycidyl ether was sprayed to (b8) evenly and applied with heat treatment at approximately 140 °C for 30 minutes to obtain the water-absorbent resin particles (b9) with the vicinity of the surface



crosslinked. The particle distribution of (b9) was almost the same as that of (b8), namely, the ratio of the fine particles with the particle size of 105 μ m or smaller was 6.4 %, and that of the fine particles with the particle size of 45 μ m or smaller was 0.9 %. For comparison, the measured results of the performance of the water-absorbent resin particles (b9) are described in the Table-2.

Comparative Example 10

The water-absorbent resin particles (b10) were obtained by removing the fine particles with the particle size of 105 μ m or smaller from the water-absorbent resin particles (b8) obtained in the Comparative Example 8. The measured results of the performance of the water-absorbent resin particles (b10) are described in the Table-2.

Comparative Example 11

100 g of acrylic acid, 0.3 g of tetraallyl oxyethane and 350 g of deionized water were placed in a 1 liter glass reactive container, and the temperature of the contents was kept at 5 °C with stirring. After introducing nitrogen to the contents to have the dissolved oxygen amount of 1 ppm or less, 1 g of 1 % aqueous solution of hydrogen peroxide and 1 g of 0.3 % aqueous solution of ascorbic acid were added to start polymerization. After the polymerization of approximately 5 hours, a hydrogel polymer was obtained.



With kneading the hydrogel polymer with an extruder with flat perforated plate, 116 g of 35 % aqueous solution of sodium hydroxide was added and kneaded uniformly, to obtain a hydrogel polymer with approximately 73 mole % of the acrylic acid was neutralized. The hydrogel polymer was dried with a drum drier with the surface temperature of 180 °C, and was pulverized to the particle distribution of the particle size of 850 μ m or smaller to obtain the water-absorbent resin particles (b11). (b11) contains 5.2 % of the fine particles with the particle size of 105 μ m or smaller, and 0.8 % of the fine particles with the particle size of 45 μ m or smaller. The measured results of the performance of the water-absorbent resin particles (b11) are described in the Table-2.

Comparative Example 12

65.4 g of acrylic acid and 78.6 g of deionized water were placed in a 200 ml flask, and 56.0 g of 48 % aqueous solution of sodium hydroxide was dropped gradually with stirring while being cooled to 20-30 °C to neutralize 74 mole % of acrylic acid. 0.2 g of N,N'-methylene bisacryl amide was dissolved in the monomer aqueous solution. Then 0.1 g of potassium persulfate was added thereto and dissolved at a room temperature, followed by introducing nitrogen gas to have the dissolved oxygen amount of 1 ppm or less in the solution.

400 g of n-hexane was placed in a 1 liter flask with a



reflux condenser installed. And after dissolving 3 g of sorbitane monostearate, nitrogen gas was introduced to have the dissolved oxygen amount of 1 ppm or less in the solution. Then while keeping the temperature at approximately 60 °C with warm bath and stirring, the above mentioned monomer aqueous solution containing potassium persulfate was dropped thereto to have polymerization for approximately 3 hours, and the polymerization was continued further for 2 hours under the reflux condition to obtain the dispersion of a spherical hydrogel polymer. By filtering the polymer dispersion to separate the hydrogel polymer and by centrifugal dehydrator, a spherical hydrogel polymer was obtained. The hydrogel polymer was dried at 90-95 °C under reduced pressure to obtain spherical water-absorbent resin particles with the particle size of 850 μm or smaller (b12). (b12) contains 6.4 % of the fine particles with the particle size of 105 μm or smaller, and the 0.9 % of fine particles with the particle size of 45 μm or smaller. The measured results of the performance of the water-absorbent resin particles (b12) are described in the Table-2.

Example 5

100 parts of the water-absorbent resin particles (b8) obtained in Comparative Example 8 and 0.05 part of dimethyl silicone oil "Shin-Etsu Silicone KF96A-100" [produced by Shin-Etsu Chemical Co., Ltd.; surface tension 20.9 dyne/cm; viscosity



100 cps; average molecular weight approximately 6,000] were placed in a V-shaped rotating mixer for mixing for 20 minutes to obtain the improved water-absorbent resin particles (a5) of the present invention having the particle distribution almost the same as that of the water-absorbent resin particles (b8). The measured results of the performance of the water-absorbent resin particles (a5) are described in the Table-2.

Examples 6, 7

The improved water-absorbent resin particles (a6) and (a7) of the present invention were obtained in the process the same as Example 5 except that the ratio of the dimethyl silicone oil "Shin-Etsu Silicone KF96A-100" to the water-absorbent resin particles (b8) in Example 5 was changed to 0.01 % and 0.1 %, respectively. The measured results of the performance of these water-absorbent resin particles are described in the Table-2.

Examples 8-10

The improved water-absorbent resin particles (a8), (a9) and (a10) of the present invention were obtained in the process the same as Example 5 except that "Shin-Etsu Silicone KF96A-100" in Example 5 was replaced by dimethyl silicone oil "Shin-Etsu Silicone KF96-50" [surface tension 20.8 dyne/cm; viscosity 50 cps; average molecular weight approximately 3,500], dimethyl silicone oil "Shin-Etsu Silicone KF96-350" [surface tension 21.1 dyne/cm; viscosity 350 cps; average molecular weight



approximately 15,000]. dimethyl silicone oil "Shin-Etsu Silicone Oil KF54" [surface tension 25.2 dyne/cm; viscosity 400 cps; average molecular weight approximately 16,000], respectively (all of the silicone oils are produced by Shin-Etsu Chemical Co., Ltd.). The measured results of the performance of these water-absorbent resin particles are described in the Table-2.

Examples 11, 12

The improved water-absorbent resin particles (a11) and (a12) of the present invention were obtained in the process the same as Example 5 except that "Shin-Etsu Silicone KF96A-100" in Example 5 was replaced by dimethyl silicone oil "Shin-Etsu Silicone KF96-5" (surface tension 19.7 dyne/cm; viscosity 5 cps; average molecular weight approximately 100), dimethyl silicone oil "Shin-Etsu Silicone KF96-3000" (surface tension 21.3 dyne/cm; viscosity 3,000 cps; average molecular weight approximately 40,000), respectively (all of the silicone oils are produced by Shin-Etsu Chemical Co., Ltd.). The measured results of the performance of these water-absorbent resin particles are described in the Table-2.

Example 13

By adding 0.02 % of silicon dioxide of 100 % of hydrophilic degree ("REOLOSIL QS-102"; produced by Tokuyama Soda Co. Ltd.) to the water-absorbent resin particles (a5) obtained in Example 5 and evenly mixing, the water-absorbent resin particles (a13) were



obtained. The measured results of the performance of the water absorbent resin particles (a13) are described in Table-2.

Examples 14-16

The improved water-absorbent resin particles (a14), (a15), (a16) of the present invention were obtained in the process the same as Example 5 except that the water-absorbent resin (b8) was replaced by the water-absorbent resins (b9), (b10), (b12), respectively. The measured results of the performance of these water-absorbent resin particles are described in Table-2.



Table-2

	water- absorbent resin particles	absorbency under pressure- free state (g/g)	absorbency under load (g/g)	absorption rate (sec)	perme- ability	gelling time (sec)
Comparative Example 8	(b8)	56	21	88	x	at least 500
Example 5	(a5)	50	21	18	⊙	42
Example 6	(a6)	56	21	25	⊙	78
Example 7	(a7)	55	22	16	⊙	64
Example 8	(a8)	56	21	18	⊙	51
Example 9	(a9)	55	20	23	⊙	76
Example 10	(a10)	56	22	20	⊙	52
Example 11	(a11)	54	18	38	○	92
Example 12	(a12)	52	16	41	○	98
Example 13	(a13)	57	22	14	⊙	38
Comparative Example 9	(b9)	52	30	55	○	148
Example 14	(a14)	52	31	8	⊙	31
Comparative Example 10	(b10)	56	21	82	△	255
Comparative Example 11	(b11)	58	22	93	x	at least 500
Example 15	(a15)	58	23	20	⊙	41
Comparative Example 12	(b12)	54	18	102	x	at least 500
Example 16	(a16)	55	19	30	⊙	55



As shown in Table-2, improved water-absorbent resin particles of the present invention and compositions containing these resin particles have superior absorption rate, excellent permeability and drastically improved gelling time without deteriorating the absorbency under pressure-free state and absorbency under load compared to the corresponding Comparative Examples.

Industrial Applicability

The improved water-absorbent resin particles of the present invention have an improved absorption rate, hygroscopic blocking rate and dust level as well as the absorbing capability of the water-absorbent resin is also maintained or improved as shown below.

1) Improvement of the absorption rate

① A high absorption rate is illustrated not only to water but also to salt solution and human body waste fluids such as urine and blood. The absorption rate is improved to be approximately $1/2$ - $1/4$ compared to water-absorbent resin particles before treatment with organic polysiloxane.

② Since liquid penetrates to the inside of particles after the surface of water-absorbent resin particles get wet evenly with the liquid, the particles absorb the liquid quickly to be gelled.



③ Even when fine particles having a small particle size are contained in a great amount in the water-absorbent resin particles, a high absorption rate is obtained.

2) Improvement of the hygroscopic blocking rate, dust generation

① Since organic polysiloxane with water repellency is affixed or adheres to the surface of the water-absorbent resin particles efficiently, the hygroscopic blocking rate is low. Therefore, the water-absorbent resin does not form blocks and provide good operativity even in the application in a high humidity.

② Since organic polysiloxane is liquid, unlike other methods to add hydrophobic fine powders, dust level can be lowered by the wetting effect. Therefore, even in dealing with water-absorbent resin particles in a great amount, fine particles are scarcely scattered to improve the operation environment to reduce the risk of the workers' inhaling the dust.

③ Since scattering is rare, the loss rate of the water-absorbent resin particles in disposable diapers can be reduced to improve productivity.

3) Maintenance or improvement of the absorbing performance

① The same or superior absorbing performance to the level before treatment is shown after the improvement with organic polysiloxane.

② In particular, when organic polysiloxane having



reactivity with water-absorbent resin before treatment, since the vicinity of the surface of the water-absorbent resin is crosslinked, the initial absorbency under load and absorption rate are improved compared to the water-absorbent resin particles before treatment. Therefore, when applied to disposable diapers, etc., the water-absorbent resin particles can rapidly absorb much urine, enduring the pressure from the weight of a baby without exuding out the absorbed urine, to provide a good surface dryness and smooth touch of the diapers.

Due to the above-mentioned advantages, the improved water-absorbent resin particles of the present invention are preferably used in hygienic materials or absorbent pads such as disposable diapers (disposable diapers for children and disposable diapers for adults), sanitary napkins, incontinence pads, mother's milk pads, underpads for operations and pet sheets.

The improved water-absorbent resin particles of the present invention are further useful in various applications utilizing particle type water-absorbent resins, including applications in contact with food such as freshness retaining materials, cooling materials and drip absorbers; materials for separating water from oil, desiccants; water retainers for plants or soil; sludge solidification agents; anti-dewing agents; water blocking materials or packing materials for construction work; and water sealing materials for electric wires or optical fiber cables and



05-07-28:01:58PM: FURUYA&CO

Obion

:38390419

47/ 51

artificial snow.



Claims:

1. Improved water-absorbent resin particles comprising water-absorbent resin particles (A) which are a crosslinked polymer of ethylenically unsaturated monomers comprising acrylic acid and/or acrylic acid salt as an essential element, treated with an organic polysiloxane (B) which is in the liquid state at an ordinary temperature, wherein

① (A) and (B) are mixed and/or reacted,

② the ratio of particles with a particle size of 10 - 1,000 μ m in (A) particles is 95 weight % or more,

③ the weight ratio of (A)/(B) is 100/(0.001-5).

2. The improved water-absorbent resin particles according to claim 1, wherein the viscosity of (B) at 25 °C is 10 - 20,000 cst and the surface tension thereof is 18 - 30 dyne/cm.

3. The improved water-absorbent resin particles according to claim 1 or claim 2, wherein (B) is a modified silicone oil having at least one functional group which can react with a carboxylic group and/or a carboxylic salt group in its molecules.

4. The improved water-absorbent resin particles according to claim 3, wherein (B) is an amino-modified silicone oil or an epoxy-modified silicone oil.

5. The improved water-absorbent resin particles according to claim 1 or claim 2, wherein the average molecular weight of (B) is 1,000 or more.



6. The improved water-absorbent resin particles according to claim 1 or claim 2, wherein the vicinity of the surface of (A) particles is further crosslinked with a crosslinking agent (C) having at least two functional groups which can react with a carboxyl group and/or a carboxylic salt group in its molecules either before the treatment of (A) with (B), at the time of the treatment (B), or after the treatment with (B).

7. The improved water-absorbent resin particles according to claim 1 or claim 2, wherein silicon dioxide fine powders (D) are further added in the amount of 0.001 - 2 weight % with respect to (A).

8. The improved water-absorbent resin particles according to claim 1 or claim 2, having the absorbing characteristic with the hygroscopic blocking rate of 20% or less under the relative humidity of 80% at 40 °C, dust level of 10 cpm or less, and the initial absorbency under load to the physiological saline solution of 20 g/g or more.



ABSTRACT

Improved water-absorbent resin particles comprising water-absorbent resin particles (A) which are a crosslinked polymer of ethylenically unsaturated monomers comprising acrylic acid and/or acrylic acid salt as an essential element, treated with an organic polysiloxane (B) which is in the liquid state at an ordinary temperature, wherein

- ① (A) and (B) are mixed and/or reacted,
- ② the ratio of particles with a particle size of 10 - 1,000 μ m in (A) particles is 95 weight % or more,
- ③ the weight ratio of (A)/(B) is 100/(0.001-5).

Since the above mentioned improved water-absorbent resin particles are superior to conventional water-absorbent resin with respect to the hygroscopic blocking rate, the dust level, also the absorbing characteristics of the water-absorbent resin including absorbing amount under a pressure-free state, absorbing amount under load, and the surface dryness after absorption are maintained or improved.

Therefore the water-absorbent resin particles of the present invention can be preferably used in various applications utilizing particle type water-absorbent resin, in particular, in hygienic materials and or absorbent pads such as disposable diapers, sanitary napkins and incontinence pads.



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP95/01076

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.⁶ B01J20/26, C08J3/12, C08J3/14, C08J3/16, C08G81/02, C08L33/02, C08F8/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Machine classification checked (classification system followed by classification system)

Int. Cl.⁶ B01J20/26, C08J3/12, C08J3/14, C08J3/16, C08G81/02, C08L33/02, C08F8/00

Classification checked after the machine classification to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926 - 1995

Kohsei Jitsuyo Shinan Koho 1971 - 1995

Electronic data base searched during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevance to claim No.
A	JP, 61-264006, A (Mitsubishi Petrochemical Co., Ltd.), November 21, 1986 (21. 11. 86), Line 7, lower right column, page 2 to line 9, upper left column, page 3 & EP, 195406, B & US, 4755560, A & DE, 3682088, G	1 - 8
A	JP, 5-70625, A (Mitsubishi Petrochemical Co., Ltd.), March 23, 1993 (23. 03. 93), Line 47, right column, page 2 to line 18, right column, page 3 (Family: none)	1 - 8

☐ Further documents are listed in the continuation of Part C.☐ See patent family group.

* Special category of cited documents

"A" Document which forms one of the documents on which the invention is based

"B" Document which has been cited in order to illustrate the invention

"C" Document which may have been cited in order to illustrate the invention

"D" Document which is cited in order to illustrate the invention

"E" Document which is cited in order to illustrate the invention

"F" Document which is cited in order to illustrate the invention

"G" Document which is cited in order to illustrate the invention

"H" Document which is cited in order to illustrate the invention

"I" Document which is cited in order to illustrate the invention

"J" Document which is cited in order to illustrate the invention

"K" Document which is cited in order to illustrate the invention

"L" Document which is cited in order to illustrate the invention

"M" Document which is cited in order to illustrate the invention

"N" Document which is cited in order to illustrate the invention

"O" Document which is cited in order to illustrate the invention

"P" Document which is cited in order to illustrate the invention

"Q" Document which is cited in order to illustrate the invention

"R" Document which is cited in order to illustrate the invention

"S" Document which is cited in order to illustrate the invention

"T" Document which is cited in order to illustrate the invention

"U" Document which is cited in order to illustrate the invention

"V" Document which is cited in order to illustrate the invention

"W" Document which is cited in order to illustrate the invention

"X" Document which is cited in order to illustrate the invention

"Y" Document which is cited in order to illustrate the invention

"Z" Document which is cited in order to illustrate the invention

"AA" Document which is cited in order to illustrate the invention

"AB" Document which is cited in order to illustrate the invention

"AC" Document which is cited in order to illustrate the invention

"AD" Document which is cited in order to illustrate the invention

"AE" Document which is cited in order to illustrate the invention

"AF" Document which is cited in order to illustrate the invention

"AG" Document which is cited in order to illustrate the invention

"AH" Document which is cited in order to illustrate the invention

"AI" Document which is cited in order to illustrate the invention

"AJ" Document which is cited in order to illustrate the invention

"AK" Document which is cited in order to illustrate the invention

"AL" Document which is cited in order to illustrate the invention

"AM" Document which is cited in order to illustrate the invention

"AN" Document which is cited in order to illustrate the invention

"AO" Document which is cited in order to illustrate the invention

Name and mailing address of the ISA/

Japanese Patent Office

Furuya Ma.

Pena PCT/ISA/210 (revised about July 1992)

Authorized officer

Telephone No.

Telex No.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☒ BLACK BORDERS

☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

☒ FADED TEXT OR DRAWING

☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING

☐ SKEWED/SLANTED IMAGES

☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS

☐ GRAY SCALE DOCUMENTS

☐ LINES OR MARKS ON ORIGINAL DOCUMENT

☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.